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(54) Title: **METHOD TO INCREASE THE CETANE NUMBER OF GAS OIL**

(57) Abstract: Method to increase the cetane number of a gas oil product based on a petroleum derived gas oil to a target cetane number Y by adding to the petroleum derived gas oil an amount of a Fischer-Tropsch derived gas oil having a higher cetane number, B, than the petroleum derived gas oil of cetane number, A, wherein the amount of added Fischer-Tropsch derived gas oil is less than the amount which would be added if linear blending is assumed.



WO 03/087273 A1

METHOD TO INCREASE THE CETANE NUMBER OF GAS OIL

The invention is directed to a method to increase the cetane number of a gas oil product based on a petroleum derived gas oil by adding to the petroleum derived gas oil an amount of a Fischer-Tropsch derived gas oil.

Commercially available blends of petroleum derived gas oil and Fischer-Tropsch derived gas oil are known. For example commercial transportation fuel formulations have been on the market, which comply with the requirements of the California Air Resources Board (CARB), and which formulations are based on a blend of gas oil as obtained in the Shell MDS Fischer-Tropsch process operating in Bintulu (Malaysia) and petroleum derived gas oils.

It is furthermore known that petroleum derived gas oils have generally a lower cetane number than gas oils derived from a Fischer-Tropsch process.

From various publications it is assumed that the cetane number of the final blend will comply with linear blending rules. See for example recent patent publication WO-A-0183648. This publication discloses that Fischer-Tropsch fuels can "upgrade" conventional fuels as predicted from simple, linear blending of the fuel parameters, i.e., as specified in "Fischer-Tropsch Wax Characterization and Upgrading Final Report" by P. P. Shah, G. C. Sturtevant, J. H. Gregor and M. J. Hurnbach, US Department of Energy, Subcontract DE-AC22-85PC80017, June 6, 1998. Furthermore from the results, as illustrated in above referred to

WO-A-0183648, one would conclude linear blending rules with regard to cetane number.

If one intends to increase the cetane number of a petroleum derived gas oil by blending with a Fischer-Tropsch derived gas oil and one assumes linear blending rules one can calculate the required volume of Fischer-Tropsch gas oil to be added.

A problem with Fischer-Tropsch derived gas oil is that they are not widely available and that the cost of preparing such gas oils is believed to be higher than the cost of preparing petroleum derived gas oil for the foreseeable future. There is thus a continuous drive to minimize the amount of Fischer-Tropsch derived gas oil in such a blend while meeting the different final product specifications.

Applicants have now surprisingly found the following more optimised method to upgrade a petroleum derived gas oil to a gas oil blend having a target cetane number using Fischer-Tropsch derived gas oil.

Method to increase the cetane number of a gas oil product based on a petroleum derived gas oil to a target cetane number Y by adding to the petroleum derived gas oil an amount of a Fischer-Tropsch derived gas oil having a higher cetane number, B, than the petroleum derived gas oil of cetane number, A, wherein the amount of added Fischer-Tropsch derived gas oil is less than the amount which would be added if linear blending is assumed.

Applicants have surprisingly found that the cetane number of a blend of petroleum derived gas oil and Fischer-Tropsch derived gas oil, in contrast to general opinion, cannot be determined by making use of linear blending assumptions. In contrast the addition of a certain volume of Fischer-Tropsch derived gas oil to a

petroleum derived gas oil results in a higher cetane number than would be expected based on linear blending rules. Thus it is possible to add less Fischer-Tropsch derived gas oil to a petroleum derived gas oil to
5 increase the cetane number of the petroleum derived gas oil to a certain target cetane number. This finding makes it possible to minimize the volume of Fischer-Tropsch gas oil in such a gas oil blend while avoiding so-called product give away with respect to cetane number.

10 It is clear that the above method would also be applicable when a blend is formulated to a certain property, which is equivalent to cetane number.

The reason why this non-linear blending property was not shown in earlier publications could be because the
15 illustrated cetane number of the blends and/or of the blending components were never actually measured. For some prior art results it is believed that the cetane number of the blends were simply calculated by applying linear blending rules on the cetane number contributions
20 of the individual blending components.

The volume fraction of Fischer-Tropsch gas oil, which is added in the method according to the invention, will be less than x , wherein x is the volume fraction that would be added if linear blending assumptions would have
25 been made according to the following equation:

$$Y = A + x(B-A).$$

The fraction x will be a value between 0 and 1 and preferably greater than 0.02. The invention is in particular directed to blends wherein the fraction x of
30 Fischer-Tropsch derived gas oil is less than 0.7 and more preferably less than 0.5 and most preferably between 0.05 and 0.3.

If a certain target cetane number Y is desired the volume fraction x is suitably determined by making use of the following non-linear blending rule, wherein Y and x are related according to the following equation:

5 $Y = A + (B-A)(-px^2 + qx),$

wherein p and q are constants such that $1.4 > q > 1.9$ and $p = q-1$ and wherein A is the cetane number of the petroleum derived gas oil and B the cetane number of the Fischer-Tropsch derived gas oil.

10 The cetane number of the petroleum derived gas oil and the Fischer-Tropsch derived gas oil as used in the method according to the invention may be measured according to the normal ASTM D613 method. Because such a method is cumbersome when performing the blending method according to the invention in a refinery environment a more
15 preferred method is by measuring the cetane number by near infrared spectroscopy (NIR) as for example described in detail in US-A-5349188. Such measurements will include the use of a correlation between the measured spectrum
20 and the actual cetane number of the sample. The underlying model is made by correlating the cetane number according to ASTM D613 of a wide variety of petroleum derived samples, Fischer-Tropsch derived gas oil samples and/or their blends with their near infrared spectral
25 data.

 Preferably the method according to the invention is embedded in an automated process control of the blending operation in for example a refinery environment. Such a process control may use so-called quality estimators
30 which will provide, by making use of a model, a real time prediction of the cetane number of the resulting blend from readily available raw process measurements, such as for example the cetane numbers as measured by NIR and the

volumetric flows. Even more preferably such a quality estimator is calibrated on-line by making use of for example the method described in detail in WO-A-0206905.

5 The Fischer-Tropsch derived gas oil may be any gas oil, which is prepared from the synthesis product of a Fischer-Tropsch synthesis. The gas oil product may be obtained by fractionation of such a Fischer-Tropsch synthesis product or obtained from a hydroconverted (hydrocracking/hydroisomerisation) Fischer-Tropsch
10 synthesis product. Examples of Fischer-Tropsch derived gas oils are described in EP-A-583836, WO-A-9714768, WO-A-9714769, WO-A-011116, WO-A-011117, WO-A-0183406, WO-A-0183648, WO-A-0183647, WO-A-0183641, WO-A-0020535, WO-A-0020534, EP-A-1101813 and US-A-6204426.

15 Suitably the Fischer-Tropsch derived gas oil will consist of at least 90 wt%, more preferably at least 95 wt% of iso and linear paraffins. The weight ratio of iso-paraffins to normal paraffins will suitably be greater than 0.3. This ratio may be up to 12. Suitably
20 this ratio is between 2 and 6. The actual value for this ratio will be determined, in part, by the hydroconversion process used to prepare the Fischer-Tropsch derived gas oil from the Fischer-Tropsch synthesis product. Some cyclic-paraffins may be present. By virtue of the
25 Fischer-Tropsch process, the Fischer-Tropsch derived gas oil has essentially zero content of sulphur and nitrogen (or amounts which are no longer detectable). These hereto-atom compounds are poisons for Fischer-Tropsch catalysts and are removed from the synthesis gas that is
30 the feed for the Fischer-Tropsch process. Further, the process does not make aromatics, or as usually operated, virtually no aromatics are produced. The content of aromatics as determined by ASTM D 4629 will typically be

below 1 wt%, preferably below 0.5 wt% and most preferably below 0.1 wt%.

The Fischer-Tropsch derived gas oil will suitably have a distillation curve which will for its majority be within the typical gas oil range: between about 150 and 400 °C. The Fischer-Tropsch gas oil will suitably have a T90 wt% of between 340-400 °C, a density of between about 0.76 and 0.79 g/cm³ at 15 °C, a cetane number greater than 70, suitably between about 74 and 82, and a viscosity between about 2.5 and 4.0 centistokes at 40 °C.

The petroleum derived gas oils are gas oils as obtained from refining and optionally (hydro)processing of a crude petroleum source. The petroleum derived gas oil may be a single gas oil stream as obtained in such a refinery process or be a blend of several gas oil fractions obtained in the refinery process via different processing routes. Examples of such different gas oil fractions as produced in a refinery are straight run gas oil, vacuum gas oil, gas oil as obtained in a thermal cracking process and light and heavy cycle oil as obtained in a fluid catalytic cracking unit and gas oil as obtained from a hydrocracker unit. Optionally a petroleum derived gas oil may comprise some petroleum derived kerosene fraction.

The straight run gas oil fraction is the gas oil fraction, which has been obtained in the atmospheric distillation of the crude petroleum refinery feedstock. It has an Initial Boiling Point (IBP) of between 150 and 280 °C and a Final Boiling Point (FBP) of between 320 and 380 °C. The vacuum gas oil is the gas oil fraction as obtained in the vacuum distillation of the residue as obtained in the above referred to atmospheric distillation of the crude petroleum refinery feedstock.

The vacuum gas oil has an IBP of between 240 and 300 °C and a FBP of between 340 and 380 °C. The thermal cracking process also produces a gas oil fraction, which may be used in step (a). This gas oil fraction has an IBP of between 180 and 280 °C and a FBP of between 320 and 380 °C. The light cycle oil fraction as obtained in a fluid catalytic cracking process will have an IBP of between 180 and 260 °C and a FBP of between 320 and 380 °C. The heavy cycle oil fraction as obtained in a fluid catalytic cracking process will have an IBP of between 240 and 280 °C and a FBP of between 340 and 380 °C. These feedstocks may have a sulphur content of above 0.05 wt%. The maximum sulphur content will be about 2 wt%. Although the Fischer-Tropsch derived gas oil comprises almost no sulphur it could still be necessary to lower the sulphur level of the petroleum derived gas oil in order to meet the current stringent low sulphur specifications. Typically the reduction of sulphur will be performed by processing these gas oil fractions in a hydrodesulphurisation (HDS) unit.

Gas oil as obtained in a fuels hydrocracker has suitably an IBP of between 150 and 280 °C and a FBP of between 320 and 380 °C.

The cetane number of the (blend of) petroleum derived gas oil (fractions) as described above is preferably greater than 40 and less than 70. Apart from increasing this cetane number of the petroleum derived gas oil other properties of the blend need to meet the required specifications. Examples of such properties are the Cloud Point, CFPP (cold filter plugging point), Flash Point, Density, Di+-aromatics content, Poly Aromatics and/or distillation temperature for 95% recovery.

Preferably the final blended gas oil product comprising the Fischer-Tropsch and the petroleum derived gas oil will have a sulphur content of at most 2000 ppmw (parts per million by weight) sulphur, preferably no more than 500 ppmw, most preferably no more than 50 or even 10 ppmw. The density of such a blend is typically less than 0.86 g/cm³ at 15 °C, and preferably less than 0.845 g/cm³ at 15 °C. The lower density of such a blend as compared to conventional gas oil blends results from the relatively low density of the Fischer-Tropsch derived gas oils. The above fuel composition is suited as fuel in an indirect injection diesel engine or a direct injection diesel engine, for example of the rotary pump, in-line pump, unit pump, electronic unit injector or common rail type.

The final gas oil blend may be an additised (additive-containing) oil or an unadditised (additive-free) oil. If the fuel oil is an additised oil, it will contain minor amounts of one or more additives, e.g. one or more additives selected from detergent additives, for example those obtained from Infineum (e.g., F7661 and F7685) and Octel (e.g., OMA 4130D); lubricity enhancers, for example EC 832 and PARADYNE 655 (ex Infineum), HITEC E580 (ex Ethyl Corporation), VELTRON 6010 (ex Infineum) (PARADYNE, HITEC and VELTRON are trademarks) and amide-based additives such as those available from the Lubrizol Chemical Company, for instance LZ 539 C; dehazers, e.g., alkoxylated phenol formaldehyde polymers such as those commercially available as NALCO EC5462A (formerly 7D07) (ex Nalco), and TOLAD 2683 (ex Petrolite) (NALCO and TOLAD are trademarks); anti-foaming agents (e.g., the polyether-modified polysiloxanes commercially available as TEGOPREN 5851 and Q 25907 (ex Dow Corning), SAG TP-325

(ex OSi), or RHODORSIL (ex Rhone Poulenc)) (TEGOPREN, SAG and RHODORSIL are trademarks); ignition improvers (cetane improvers) (e.g., 2-ethylhexyl nitrate (EHN), cyclohexyl nitrate, di-tert-butyl peroxide and those disclosed in
5 US-4,208,190 at column 2, line 27 to column 3, line 21); anti-rust agents (e.g., that sold commercially by Rhein Chemie, Mannheim, Germany as "RC 4801", a propane-1, 2-diol semi-ester of tetrapropenyl succinic acid, or polyhydric alcohol esters of a succinic acid derivative,
10 the succinic acid derivative having on at least one of its alpha-carbon atoms an unsubstituted or substituted aliphatic hydrocarbon group containing from 20 to 500 carbon atoms, e.g., the pentaerythritol diester of polyisobutylene-substituted succinic acid); corrosion
15 inhibitors; reodorants; anti-wear additives; anti-oxidants (e.g., phenolics such as 2,6-di-tert-butyl-phenol, or phenylenediamines such as N,N'-di-sec-butyl-p-phenylenediamine); and metal deactivators.

The additive concentration of each such additional
20 component in the additivated fuel composition is preferably up to 1 %w/w, more preferably in the range from 5 to 1000 ppmw, advantageously from 75 to 300 ppmw, such as from 95 to 150 ppmw.

The invention will be illustrated by means of the
25 following non-limiting examples.

Example

In this Example use is made of a petroleum derived gas oil and two Fischer-Tropsch derived gas oils in the absence of any additives (FT1 and FT2) having the
30 properties as listed in Table 1. The cetane number was measured according to the CFR Cetane Engine method, ASTM D 613.

Table 1

	Petroleum derived gas oil	Fischer-Tropsch derived gas oils	
PROPERTIES		FT1	FT2
DENSITY @ 15 °C			
(IP365/ASTM D4052) g/cm ³	0.8503	0.776	0.7782
DISTILLATION			
(IP123/ASTM D86)			
IBP °C	201.0	183.5	186.5
10%	244.0	214.1	216.5
20%	259.5	228.4	234.0
30%	270.5	243.6	247.0
40%	281.0	259.5	261.0
50%	290.0	275.4	273.0
60%	299.5	291.2	285.0
70%	309.5	306.9	297.5
80%	321.0	322.9	310.5
90%	337.5	340	324.5
95%	351.0	351.3	333.5
FBP	363.5	359	339.5
CETANE NUMBER ASTM D613	51.1	77.3	75.8
Kinematic viscosity at 100 °C (cSt)		3.103	2.665
(IP71/ASTM D445)			
SULPHUR (IP373) ppm M	400	0	<5
CARBON wt%	86.9	84.9	84.6
HYDROGEN wt%	13.2	15	15

In order to increase the cetane number of 51.1 of the petroleum derived gas oil to a target cetane number Y as listed in Table 2 different amounts of Fischer-Tropsch

derived gas oil FT1 had to be added. From Table 2 it is clear that this amount is less than the volume, which would have been added if linear blending were assumed.

Table 2

Target cetane number Y	Fraction x of FT1 added to petroleum derived gas oil	Fraction of FT1 added if linear blending was assumed
59.6	0.15	0.31
63.3	0.30	0.47
69.3	0.50	0.69
73.1	0.7	0.84

From the results shown in Table 2 it is clear that by using the method according to the present invention considerably less Fischer-Tropsch derived gas oil needs to be added to a petroleum derived gas oil when blending such gas oils to reach a certain target cetane number. This effect is especially pronounced at values for x smaller than 0.5.

Similar results were obtained when the second Fischer-Tropsch derived gas oil (FT2) was used to increase the cetane number of the blend (see Table 3).

Table 3

Target cetane number Y	Fraction x of FT2 added to petroleum derived gas oil	Fraction of FT2 added if linear blending was assumed
57.3	0.15	0.23
62.3	0.30	0.44
65.4	0.5	0.56
68.8	0.7	0.7

C L A I M S

1. Method to increase the cetane number of a gas oil product based on a petroleum derived gas oil to a target cetane number Y by adding to the petroleum derived gas oil an amount of a Fischer-Tropsch derived gas oil having a higher cetane number, B, than the petroleum derived gas oil of cetane number, A, wherein the amount of added Fischer-Tropsch derived gas oil is less than the amount which would be added if linear blending is assumed.

2. Method according to claim 1, wherein the volume fraction of Fischer-Tropsch gas oil is less than x, wherein x is the volume fraction that would be added if linear blending assumptions would have been made according to the following equation:

$$Y = A + x(B-A),$$

3. Method according to any one of claims 1 or 2, wherein a volume fraction x is added as Fischer-Tropsch derived gas oil in order to increase the cetane number to target value Y, wherein Y and x are related according to the following equation:

$$Y = A + (B-A)(-px^2 + qx),$$

where p and q are constants such that $1.4 > q > 1.9$ and $p = q-1$ and wherein A is the cetane number of the petroleum derived gas oil and B the cetane number of the Fischer-Tropsch derived gas oil.

4. Method according to claim 3 wherein, x is greater than 0.02 and less than 0.7.

5. Method according to claim 4, wherein x is less than 0.5.

6. Method according to any one of claims 1-5, wherein the cetane number, A, of the petroleum derived gas oil is greater than 40 and less than 70.

5 7. Method according to any one of claims 1-6, wherein the cetane number of the petroleum derived gas oil is measured by making use of near infrared spectroscopy.

8. Gas oil product comprising a gas oil blend as obtained by the method according to any one of claims 1-7, one or more additives, less than 500 ppmw
10 sulphur and having a density of less than 0.86 g/cm^3 at 15°C .

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 03/03927

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C10L1/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C10L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	US 2002/020107 A1 (OHI JAMES M ET AL) 21 February 2002 (2002-02-21) paragraph '0042! - paragraph '0043! -/--	1-6

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

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INTERNATIONAL SEARCH REPORT

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP 03/03927

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